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著者	Hirosawa Ichiro
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Crystal structure of $A_xB_{3-x}C_{60}$ compounds

Ichiro Hirosawa

NEC Corporation

Abstract

Chap. I. Introduction

The 1990 breakthrough in fullerene production led to the synthesis of new carbon-based compounds. C_{60} is the most interesting, because superconducting compounds have been found in alkali doped C_{60}. I also joined the race to synthesize new compounds with a higher Tc, and started a more systematic study to elucidate correlation between the Tc and the crystal structure of alkali-doped C_{60} superconductors to find the orientation in order to synthesize new compounds with higher Tc.

Chap. II. Synthesizing alkali-doped C_{60} compounds.

The doping of alkali metals into C_{60} occurs on direct reaction between pristine C_{60} and alkali metal ingots. Stoichiometrically weighted C_{60} and alkali metal ingots are introduced into a Ta crucible. Then the crucible is sealed in a glass tube with He gas at 500 Torr. The reaction occurs on heating at 400°C.

Chap. III. Stability of compounds and site selectivity of doped alkali ions

I tried to synthesize binary and ternary alkali metal doped C_{60} compounds to investigate as many compounds as possible, and found that stable compounds are classified into two groups of $(Li_xNa_{2-x})(Rb_yCs_{1-y})C_{60}$ $(0<x<2, 0<y<1)$ and $K_xRb_yCs_{3-x-y}C_{60}$ $(0<x,y<3, 1<x+y<3)$. These compounds are superconducting without $Li_2(Rb_xCs_{1-x})C_{60}$. Then it was found that the dependence of Tc on lattice constant of $Na_2(Rb_xCs_{1-x})C_{60}$ is different from that of $K_xRb_yCs_{3-x-y}C_{60}$. In addition, the characteristic occupation behavior of alkali ions that the larger ions preferentially occupy octahedral interstitial sites was found by X-ray diffraction.

Chap. IV. C_{60} orientation

Three types of C_{60} orientation were found by X-ray diffraction. In $K_xRb_yCs_{3-x-y}C_{60}$ compounds, alkali ions in tetrahedral interstitial sites are surrounded by hexagons of the nearest C_{60}. The C_{60} orientation of Na containing compounds is quite different. $Na_2(Rb_xCs_{1-x})C_{60}$ has the order-disorder phase transition of C_{60} orientation. In low temperature phase eight double bonds of C_{60} face to pentagons of neighboring C_{60}, and C_{60} is rotating freely in high temperature phase. The C_{60}

orientation of non-superconducting compound Li_2CsC_{60} is also different from both $K_xRb_yCs_{3-x-y}C_{60}$ and $Na_2(Rb_xCs_{1-x})C_{60}$. No order-disorder transition is observed in the range of 10-450K, and C_{60} of Li_2CsC_{60} is random even at 10K.

Chap. V. Location of alkali ions in octahedral interstitial site

The possibility that alkali ions do not center on octahedral interstitial site was suggested by extremely larger Debye-Waller factor of O-site ion than that of T-site ion. Then EXAFS measurements were taken to clarify location of alkali ions in octahedral interstitial sites. When Rb ion is located on center of O-sites, interatomic distance of Rb-C and coordination number of K_2RbC_{60} should be 3.72A and 12, respectively. However, interatomic distance of Rb-C and coordination number of K_2RbC_{60} are determined to be 3.3A and 3.4. This result indicates that the Rb ion shifts in the <111> direction from the center of O-site.

Chap. VI. Energetics of site selectivity of $A_xB_{3-x}C_{60}$ compounds

Site selectivity of alkali ions in $A_xB_{3-x}C_{60}$ is discussed with cohesive energy model of these compounds. It is assumed that cohesive energies are composed of Coulomb interaction (Madelung energy), repulsions of C_{60} to alkali ions in tetrahedral and octahedral interstitial sites and C_{60} intermolecular interaction. Madelung energy is calculated by Ewald sum, and Born-Mayer type potential $b \times \exp(-r/\rho)$ is adopted as repulsion between C_{60} and alkali ion. Parameters b and ρ are determined from compressibilities and lattice constants of K_3C_{60}, Rb_3C_{60} or GIC. The C_{60} intermolecular interaction is treated to be sum of L-J potential between carbon atoms distributed on two spheres. In this approximation cohesive energies of site selective alignments are always smaller than those of random occupations of alkali ions.

Chap. VII. Energetics of C_{60} orientation

It is also considered how C_{60} orientation is determined. In this discussion C_{60} intermolecular interaction and repulsions between alkali ions and carbons are considered. C_{60} intermolecular interaction proposed by Lu (J. P. Lu et al., Phys. Rev. Lett. 68, 1551 (1992)) was adopted, and repulsions of 12 alkali ions surrounding C_{60} were taken into consideration. This model can explain C_{60} orientations in $K_xRb_yCs_{3-x-y}C_{60}$ and $Na_2(Rb_xCs_{1-x})C_{60}$. However, the random orientation of C_{60} in Li_2CsC_{60} cannot be recognized.

Chap. VIII. Summary

The study is summarized in this chapter. The most important point of this study is that electronic character of these compounds are largely affected by C_{60} orientation.